AFRL-AFOSR-VA-TR-2017-0067

TU(R)NING WEAKNESS TO STRENGTH - MECHANOMUTABLE BIOINSPIRED MATERIALS

Markus Buehler
MASSACHUSETTS INSTITUTE OF TECHNOLOGY
77 MASSACHUSETTS AVE
CAMBRIDGE, MA 02139-4301

04/03/2017
Final Report

Air Force Research Laboratory
AF Office Of Scientific Research (AFOSR)/RTA1

Arlington, Virginia 22203
Air Force Materiel Command

REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

1. REPORT DATE *(DD-MM-YYYY)*	2. REPORT TYPE	3. DATES COVERED *(From - To)*
03-04-2017	Final Performance	01 Sep 2011 to 31 Aug 2016

4. TITLE AND SUBTITLE
TU(R)NING WEAKNESS TO STRENGTH - MECHANOMUTABLE BIOINSPIRED MATERIALS

5a. CONTRACT NUMBER

5b. GRANT NUMBER
FA9550-11-1-0199

5c. PROGRAM ELEMENT NUMBER
61102F

6. AUTHOR(S)
Markus Buehler

5d. PROJECT NUMBER

5e. TASK NUMBER

5f. WORK UNIT NUMBER

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)
MASSACHUSETTS INSTITUTE OF TECHNOLOGY
77 MASSACHUSETTS AVE
CAMBRIDGE, MA 02139-4301 US

8. PERFORMING ORGANIZATION REPORT NUMBER

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)
AF Office of Scientific Research
875 N. Randolph St. Room 3112
Arlington, VA 22203

10. SPONSOR/MONITOR'S ACRONYM(S)
AFRL/AFOSR RTA1

11. SPONSOR/MONITOR'S REPORT NUMBER(S)
AFRL-AFOSR-VA-TR-2017-0067

12. DISTRIBUTION/AVAILABILITY STATEMENT
A DISTRIBUTION UNLIMITED: PB Public Release

13. SUPPLEMENTARY NOTES

14. ABSTRACT
They used a combination of multiscale modeling and experimental synthesis to understand the behavior of this heterologous-expressed protein from the nanoscale to the macroscale. They built a bottom-up molecular-based model, which includes electronic -based density functional theory calculations, atomistic simulation of the nanoscale properties with replica exchange molecular dynamics, and an elastic network model for describing the macroscale behavior at different pHs. This multiscale modeling supports the experimental synthesis of a photo-crosslinked Nvjp-1 hydrogel by proving both the nanoscale mechanisms and mechanical behavior predictions.

15. SUBJECT TERMS
hybrid materials, low density materials

16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT	18. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON
a. REPORT	b. ABSTRACT	c. THIS PAGE			GORETTA, KENNETH
Unclassified	Unclassified	Unclassified	UU		19b. TELEPHONE NUMBER *(Include area code)* 703-696-7349

Standard Form 298 (Rev. 8/98)
Prescribed by ANSI Std. Z39.18

Final Report

To:	technicalreports@afosr.af.mil
Subject:	Final Report
Contract/Grant Title:	Tu(r)ning weakness to strength: Mechanomutable bioinspired materials
Contract/Grant #:	FA9550-11-1-0199
Program Manager:	GORETTA, KENNETH C DR.; 04 USAF AFMC AFOSR/RTA
	kenneth.goretta@us.af.mil
Reporting Period:	09/01/2011 to 08/31/2016
PI:	Markus J. Buehler, Massachusetts Institute of Technology

Archival publications (published) during reporting period:

- C.-C. Chou, F. J. Martin-Martinez, Z. Qin, P. B. Dennis, M. K. Gupta, R. R. Naik, M. J. Buehler "Ion Effect and Metal-Coordinated Crosslinking for Multiscale Design of Nereis Jaw Inspired Mechanomutable Materials" ACS Nano, Article ASAP, 2017
- C.-C. Chou, E. Lepore, P. Antonaci, N. Pugno, M.J. Buehler, "Mechanics of trichocyte alpha-keratin fibers: Experiment, theory and simulation," Vol. 30, pp. 26-35, 2015
- Z. Qin, M.J. Buehler, "Nonlinear viscous water at nanoporous two-dimensional interfaces resists high-speed flow through cooperativity," Vol.15(6), pp. 3939-44, 2015
- T. Al-Mulla, Z. Qin, M.J. Buehler, "Crumpling Deformation Regimes of Monolayer Graphene on Substrate: A Molecular Dynamics Study," *Journal of Physics: Condensed Matter*, Vol. 27, 345401, 2015
- Z. Qin, B.G. Compton, J.A. Lewis, M.J. Buehler, "Structural optimization of 3D-printed synthetic spider webs for high strength," *Nature Communications*, Vol. 6, 7038, 2015
- R. Mirzaeifar, Z. Qin, M.J. Buehler, "Mesoscale Mechanics of Twisting Carbon Nanotube Yarns," *Nanoscale*, Vol. 7, 5435-5445, 2015
- G. Jung, Z. Qin, M.J. Buehler, "Molecular mechanics of polycrystalline graphene with enhanced fracture toughness," *Extreme Mechanics Letters*, Vol. 2, pp. 52-59, 2015
- R. Mirzaeifar, L. Dimas, Q. Qin, M.J. Buehler, "Defect-tolerant Bioinspired Hierarchical Composites: Simulation and Experiment," *ACS Biomaterials Science & Engineering*, Vol. 1(5), pp 295–304, 2015
- T. Al-Mulla, M.J. Buehler, "Folding creases through bending," *Nature Materials*, Vol. 14, pp. 466-468, 2015
- Z. Qin, M. Taylor, M. Hwang, K. Bertoldi, M.J. Buehler, "Effect of Wrinkles on the Surface Area of Graphene: Toward the Design of Nanoelectronics," *Nano Letters*, Vol. 14(11), pp. 6520-6525, 2014
- S. Lin, M.J. Buehler, "Thermal Transport in Monolayer Graphene Oxide: Atomistic Insights into Phonon Engineering through Surface Chemistry," *Carbon*, Vol. 77, 351-359, 2014

- M. Solar, Z. Qin, M.J. Buehler, "Molecular mechanics and performance of crosslinked amorphous polymer adhesives," *Journal of Materials Research*, Vol. 29(9), 1077-1085, 2014
- M. Solar, M.J. Buehler, "Tensile Deformation and Failure of Amyloid and Amyloid-Like Protein Fibrils," *Nanotechnology*, Vol. 25(10), 105703, 2014
- Z. Qin, N. Pugno, M.J. Buehler, "Mechanics of fragmentation of crocodile skin and other thin films," *Scientific Reports*, Vol. 4, article # 4966, 2014
- C.-T. Chen, C. Chuang, J. Cao, V. Ball, M.J. Buehler, "Excitonic effects from geometric order and disorder explain broadband optical absorption in eumelanin," *Nature Communications*, Vol. 5, article # 3859, 2014
- C.-T. Chen, S. Ghosh, C.M. Reddy, M.J. Buehler, "Molecular mechanics of elastic and bendable caffeine co-crystals," *Physical Chemistry Chemical Physics*, Vol. 16(26), 13165-13171, 2014
- S. Lin, M.J. Buehler, "Thermal Transport in Monolayer Graphene Oxide: Atomistic Insights into Phonon Engineering through Surface Chemistry," *Carbon*, Vol. 77, 351-359, 2014
- M. Solar, Z. Qin, M.J. Buehler, "Molecular mechanics and performance of crosslinked amorphous polymer adhesives," *Journal of Materials Research*, Vol. 29(9), 1077-1085, 2014
- A. Kalinowski, P.N. Yaron, Z. Qin, S. Shenoy, M.J. Buehler, M. Losche, K.N. Dahl, "Interfacial binding and aggregation of lamin A tail domains associated with Hutchinson-Gilford progeria syndrome," *Biophysical Chemistry*, Vol. 195, 43-48, 2014
- T. Verho, M.J. Buehler, "Flaw tolerance promoted by dissipative deformation mechanisms between material building blocks," *Philosophical Magazine Letters*, Vol. 94, 592-600, 2014.
- A.K. Nair, A. Gautieri, M.J. Buehler,"Role of intrafibrillar collagen mineralization in defining the compressive properties of nascent bone," *Biomacromolecules*, Vol. 15(7), pp. 2494-2500, 2014
- W. Yang, V. Sherman, B. Gludovatz, M. Mackey, E.A. Zimmermann, E.H. Changm E. Schaible, Z. Qin, M.J. Buehler, R. Ritchie, M. Meyers, "Protective Role of Arapaima gigas Fish Scales: Structure and Mechanical Behavior," *Acta Biomaterialia*, Vol. 10(8), 3599-3614, 2014
- L.S. Dimas, M.J. Buehler, "Modeling and Manufacturing of Bio-inspired Composites with Tunable Fracture Mechanical Properties," *Soft Matter*, Vol.10(25), 4436-4442, 2014
- S.W. Chang, M.J. Buehler, "Molecular biomechanics of collagen molecules," *Materials Today*, Vol. 17(2), 70-76, 2014
- M. Solar, M.J. Buehler, "Tensile Deformation and Failure of Amyloid and Amyloid-Like Protein Fibrils," *Nanotechnology*, Vol. 25(10), 105703, 2014
- T. Giesa, N. Pugno, J.Y. Wong, D.L. Kaplan, M.J. Buehler, "What's Inside the Box? – Length-Scales that Govern Fracture Processes of Polymer Fibers," *Advanced Materials*, Vol. 26(3), 412-417, 2014
- Z. Qin, L. Dimas, D. Adler, G. Bratzel, M.J. Buehler, "Biological materials by design," *J. Phys. Cond. Mattter*, Vol. 26(7), article # 073101, 2014
- F. LIbonati, A. Nair, L. Vergani, M.J. Buehler, "Mechanics of collagen-hydroxyapatite model nanocomposites," *Mechanics Research Communications*, Vol. 58, 17-23, 2014
- A. Nair, F. Libonati, Z. Qin, L. Dimas, M.J. Buehler, "Mechanical and interface properties of biominerals: Atomistic to coarse grained modeling," In: Biomineralization Handbook:

Characterization of biomineral and biomimetic materials (editor: Elaine DiMasi), CRC Press, 2014

- G. Bratzel, Z. Qin, M.J. Buehler, "Viscoelastic relaxation time and structural evolution during length contraction of spider silk protein nanostructures," *MRS Communications*, Vol. 3(3), pp. 185-190, 2013
- A. Tarakanova, M.J. Buehler, "Molecular modeling of protein materials: case study of elastin," *Modelling and Simulation in Materials Science and Engineering*, Vol. 21(6), paper # 063001, 2013
- V. Ball, J. Gracio, M. Vila, M. Singh, M. Michel, J. Bour, V. Toniazzo, D. Ruch, M.J. Buehler, "Comparison of synthetic eumelanin formed in the presence of oxygen and Cu2+ cations as oxidants," *Langmuir*, Vol. 29(41), pp. 12754-12761, 2013
- O. Tokareva, M. Jacobson, M.J. Buehler, J. Wong, D. Kaplan, "Structure-Function-Property-Design Interplay in Biopolymers: Spider Silk," *Acta Biomaterialia*, Vol. 10, 1612–1626, 2014
- Z. Qin, M.J. Buehler, "Molecular mechanics of mussel adhesion proteins," *J. Mech. Phys. Solids*, Vol.62, 19-30, 2014
- M.J. Buehler, "Materials by design-A perspective from atoms to structures", Vol. 38, pp. 169-176, 2013
- M.J. Buehler, "Mechanical Players-The Role of Intermediate Filaments in Cell Mechanics and Organization," *Biophysical J.*, Vol. 105(8), pp. 1733-1734, 2013
- S. Lin, M.J. Buehler, "Mechanics and molecular filtration performance of graphyne nanoweb membranes for selective water purification," *Nanoscale*, Vol. 5, 11801-11807, 2013

- Z. Qin, M.J. Buehler, "Cooperativity governs the size and structure of biological interfaces," *J. Biomechanics*, Vol. 45(16), pp. 2778-2783, 2012
- G. Gronau, S. Tarakkad Krishnaji, M.E. Kinahan, T. Giesa, J.Y. Wong, D.L. Kaplan, M.J. Buehler, "A review of combined experimental and computational procedures for assessing biopolymer structure–process–property relationships," *Biomaterials*, Vol. 33(33), pp. 8240-8255, 2012
- Z. Qin, M.J. Buehler, "Bio-inspired graphene nano-gut," *J. Applied Mechanics*, accepted for publication
- Z. Qin, M.J. Buehler, "Mechanical properties of crosslinks controls failure mechanism of hierarchical intermediate filament networks," *Theoretical and Applied Mechanics Letters*, Vol. 2(1), article # 014005, 2012
- C.C. Chou, M.J. Buehler, "Molecular mechanics of disulfide bonded alpha-helical protein filaments," *BioNanoScience*, accepted for publication
- J. Wong, J. McDonald, M. Taylor-Pinney, D.I. Spivak, D. Kaplan, M.J. Buehler, "Materials by Design: Merging Proteins and Music," *Nano Today*, DOI: 10.1016/j.nantod.2012.09.001, 2012
- J. Zang, S. Ryu, N. Pugno, Q. Wang, Q. Tu, M. J. Buehler, and X. Zhao, "Multifunctionality and control of crumpling and unfolding of large-area graphene," *Nature Materials*, Vol. 12(4), pp. 321-325, 2013
- S. Cranford, J. De Boer, C. van Blitterswijk, M.J. Buehler, "Materiomics: an -omics approach to biomaterials research," *Advanced Materials*, 2013
- G. Gronau, Z. Qin, M.J. Buehler, "Effect of sodium chloride on the structure and stability of spider silk's N-terminal protein domain," *Biomaterials Science*, 2013

Book (published) during reporting period

- S. Cranford, N. Pugno, M.J. Buehler, "Silk and Web Synergy: The Merging of Material and Structural Performance," in: Biotechnology of Silk (editors: Tetsuo Asakura and Thomas A. Miller), Springer, 2014

Students that were supported throughout the years, students graduated

- Zhao Qin (Research Scientist)
- Francisco Martin-Martinez (Research Scientist)
- Jingjie Yeo (Postdoctoral Fellow)
- Shu-Wei Chang (PhD Graduated).
- Chia-Ching Chou (PhD Graduated).
- Chun-Teh Chen (PhD. Graduated)
- Dieter B. Brommer (MSc Graduated).
- Gang Seob Jung (PhD Student)
- Isabelle Su (MSc Student)
- Talal Al-Mulla (MSc Student)
- Maria Tou (UROP Student)

Awards that I or others funded by the project have won

- Feynman Prize, Theory, 2016;
- Outstanding Young Scientist Award, NANOSMAT Society, 2016;
- Fellow, NANOSMAT Society, 2016;
- Most Cited Paper Award (2009-2015), International Journal of Applied Mechanics (IJAM), 2016;
- Fellow, AIMBE, 2015;
- ASME Journal of Applied Mechanics Award 2014;
- Robert Lansing Hardy Award 2013 (TMS);
- TMS Structural Materials Division Best Paper Award 2013;
- MRS Outstanding Young Investigator Award 2012;
- IEEE Holm Conference Antler Lecture Award 2012;
- SES Young Investigator Medal 2012;
- Alfred Noble Prize 2011;
- Thomas J.R. Hughes Young Investigator Award 2011;
- Leonardo Da Vinci Award 2011 (ASCE);
- Stephen Brunauer Award 2011 (ACS);
- Rossiter W. Raymond Memorial Award 2011 (AIME).

Talks given related to the project (only Invited are listed)

- "Turning weakness to strength," Department of Integrative Biology, University of Guelph, Canada September2 011
- "From atoms to structures – how spiders turn weakness into strength," University of Colorado,Boulder Mechanics Seminar Series, Boulder, CO September 2011
- "From atoms to structures – how spiders turn weakness into strength," Applied Mechanics Colloquium, School of Engineering and Applied Sciences, Harvard University, Cambridge, MA September 2011

- “From atoms to structures – how spiders turn weakness into strength,” Department of Mechanical Engineering University of Michigan, Ann Arbor, MI September 2011
- “Tu(r)ning weakness to strength – from atoms to spider webs,” Mechanical Engineering Seminar, University of Houston, TX October 2011
- “Nonlinear behavior of silk minimizes damage and begets spider web robustness from the molecules up,” 2011 MSM Consortium/NHLBI Systems Biology Meeting: Interagency Modeling and Analysis Group, National Institutes of Health (NIH) Invited poster presentation October 2011
- “Turning weakness to strength: How spiders spin silks of superhero strength,” CECAM Workshop “Perspectives and challenges of simulations at bio-materials interfaces,” University of Bremen, Germany October 2011
- “Modeling and designing new materials based on chemical structures,” LANXESS Global Leadership Forum, Cambridge, MA # # Other speakers included: Nobel Laureate R. Schrock, MIT October 2011
- “From atoms to structures, turning weakness to strength,” Materials Day 2011, Cambridge, MA October 2011
- “How weakness is turned to strength in the design of biological materials and structures,” Micro- and Nanoscale Processing of Biomedical Materials, Materials Research Society Fall Meeting 2011, Boston, MA November 2011
- “Protein mechanics from molecules to spider webs,” Department of Biochemistry, MDNJ-Robert Wood Johnson Medical School, Piscataway, NJ November 2011
- “Tu(r)ning weakness to strength: Mechanics of Spider Silk, from Atoms to the Web,” ASME 2011 International Mechanical Engineering Congress & Exhibition, Denver, CO November 2011
- “Turning weakness into strength,” 4th International Conference on the Mechanics of Biomaterials and Tissues, Hawai December 2011
- “Hierarchical mechanics of bionanomaterials,” 2011 International Workshop, -- US Office of Naval Research (ONR) and SEACOAT, Las Vegas, NV December 2011
- "Biomateriomics," Materials Genome Initiative - Materials By Design Town Hall, Brown University, Providence, RI March 2012
- “From atoms to structures – how spiders turn weakness into strength,” 2012 NANOSMAT USA Conference, Tampa, FL March 2012
- “From Atoms to Structures - How Spiders Turn Weakness into Strength,” Bio-inspired Materials, Potsdam, Germany March 2012
- “Nonlinear behaviour of silk minimizes damage and begets spider web robustness from the molecules up,” TMS 2012 Annual Meeting & Exhibition, Orlando, FL March 2012
- “From Atoms to Structures–How Spiders turn Weakness into Strength,” Materials Research Society Spring Meeting 2012, San Francisco, CA April 2012
- “From Atoms to Structures—Turning Weakness into Strength,” Materials Research Society Spring Meeting 2012, San Francisco, CA April 2012
- “Interfacial Mechanics from a Molecular Perspective,” Materials Research Society Spring Meeting 2012, San Francisco, CA April 2012
- “Computational materials science – From Atoms to Structures,” IEEE Holm Conference, Portland, OR Keynote Lecture September 2012
- “Biomateriomics — from atoms to structures,” ASME Webinar October 2012
- “Materials by design,” MIT Club of Germany Part of delegation with MIT Chancellor Eric Grimson October 2012

- “From atoms to structures – how spiders turn weakness into strength,” Society of Engineering Science Meeting, Atlanta, GA Keynote Lecture October 2012
- “Hierarchical mechanics of silk and other biopolymers,” Symposium R: Fundamentals of Assembly in Biomolecular and Biomimetic Systems, MRS Fall Meeting 2012, Boston, MA. November 2012
- "Materials By Design," Civil and Environmental Engineering, Worcester Polytechnic Institute, Worcester, MA November 2012
- "Materials By Design," Civil and Environmental Engineering, George Washington University,
- Washington, DC November 2012
- "Computational Biomaterials Science: Materials By Design," Institut für Materialprüfung, Werkstoffkunde und Festigkeitslehre (IMWF), Stuttgart, Germany January 2013
- "Biomateriomics," ASME 2013 2nd Global Congress on NanoEngineering for Medicine and Biology Plenary Lecture February 2013
- "Bottom-up molecular models of hierarchical mineralized tissues: Structure, mechanics and biology," APS Spring Meeting, Baltimore, MD March 2013
- "Materials By Design: Silk and Silk-Like Protein Materials," DPG Spring Meeting, Regensburg, Germany March 2013
- "Hierarchical Composites from Simple Building Blocks: Computation, Theory and Experiment," TMS Meeting, San Antonio, TX March 2013
- "Materials by Design: Silk and Silk-Like Protein Materials," TMS Meeting, San Antonio, TX March 2013
- "Structure and Mechanics of Silk and Silk-inspired Materials," Chemical Physics Seminar, California Institute of Technology, Pasadena, CA April 2013
- "Pulling and squeezing squishy silk," Squishy Physics & Pizza Seminar Series, Harvard University April 2013
- "Overview of Materiomics: Impact on Biological and Non-Biological Systems," 2013 German-American Frontiers of Engineering Symposium, National Academy of Engineering, Irvine, California Plenary Lecture April 2013
- "Fragility: What is it That Makes Materials and Ecosystems Prone to Fracture," BBC World Programme: "The Forum" Radio show; M.J. Buehler with Barbara Kingsolver and David Goulson May 2013
- "Structure and Mechanics of Silk and Silk-inspired Materials," Canadian Society for Chemistry Conference: New Trends in Protein Science May 2013
- "Biomimicry, materials and additive manufacturing," Global Biomimicry Conference and 7th Annual Biomimicry Education Summit, Boston, MA June 2013
- "Hierarchical Biocomposites By Design," 19th International Conference on Composite Materials (ICCM19), Montreal, Canada Keynote Lecture July 2013
- "Computational Biomaterials Science," 12th U.S. National Congress on Computational Mechanics (USNCCM12), Raleigh, NC Plenary Talk July 2013
- "Lessons from molecular modeling of spider silk, experimenta and theory," Gordon Research Conference: Elastin, University of New England, Biddeford, ME July 2013
- "From molecular structure to material properties: Simulation, synthesis, testing," ExxonMobil Polymer Modeling Minisymposium, Clinton, NJ July 2013
- "Hierarchical Nanomaterials for High-Performance Engineering Applications," BOSCH GmbH. Schillerhoehe, Germany August 2013
- "Biomaterials By Design," Mechanics: Modeling, Experimentation, Computation Seminar Series, MIT Mechanical Engineering, 2013 September 2013

- "Bioinspired Materials," North Carolina A&T University, College of Engineering Dean's Distinguished Speaker Seminar Series, Greensboro, NC September 2013
- "Biomateriomics," NEW.Mech Workshop, Boston, MA October 2013
- "Bioinspired materials: Hierarchies from nano to macro and analogies between materials and music," Lincoln Laboratory, Lexington, MA
- "Biomaterials by Design—Modeling, Synthesis, Testing," Army Research Office 2013 Workshop: Issues and Challenges in Nanomanufacturing, Additive Manufacturing, and Advanced Manufacturing, Alumni Center, North Carolina State University, Raleigh, NC October 2013
- "3D Printing of "Artificial Bone" Composite Material," 2013 MIT Research and Development Conference, Cambridge, MA November 2013
- "Bioinspired Materials," EMD-Millipore Workshop, Cambridge, MA January 2014
- "Benign Materials by Design," Environmental Chemistry and Microbiology Student Symposium (ECMSS), The Pennsylvania State University, State College, PA March 2014
- "Biomateriomics: Multiscale Materials By Design," OSU Materials Week, May 8, 2014 May 2014
- "Biomateriomics of Functional & Tunable Fibers," 2014 GRC Bioinspired Materials, June 22-27, 2014 June 2014
- "The Interagency Modeling and Analysis Working Group on Integrated Multiscale Biomaterials Experiment and Modeling," 2014 Multiscale Modeling Consortium Meeting, September 5-6, 2014, Bethesda, MD (plenary lecture, with Guy Genin/WUSTL) September 2014
- "Making Nano Big," Distinguished Seminar, Northeastern University, Department of Civil and Environmental Engineering September 2014
- "Seeing Music in Nature," Cardinal and Gray/Emma Rogers Society Fall Lecture and Luncheon October 23, 2014 October 2014
- "Making Nano Big," Collaboratory on Mathematics for Mesoscopic Modeling of Materials (CM4) November 2014
- "Biologically inspired materials & structures for strength and toughness," MIT-CEE Research Speed Dating Day, Feb. 20, 2015, Cambridge, MA February 2015
- "Making Nano Big," Colloquia on Theoretical and Applied Mechanics, Northwestern University, March 6, 2015, Chicago, IL March 2015
- "Materials by Design," Active Matter Summit, April 24-25, 2015, Cambridge, MA April 2015
- "Integrating Modeling & Experimental Approaches in Biomaterials Designs," Interagency Modeling and Analysis Group, National Institutes of Health (NIH), May 30, 2015 May 2015
- "Biomateriomics: Bio-inspired composites, additive manufacturing, and printing models," Preconference Symposium: Intelligent design: multi-scale modeling of cells, tissues, and organs, Tissue Engineering and Regenerative Medicine International Society (TERMIS) World Congress, Sept. 7-11, 2015, Boston, MA September 2015
- "Engineering a Resilient Future," Boston: Sink or Swim, Boston Athenæum, Sept. 21, 2015, Boston, MA September 2015
- "Engineering a Resilient Future," LGO Operating Committee Meeting, Sept. 30, 2015, Cambridge, MA September 2015
- "Multiscale materials by design - connecting simulation, design, synthesis," Structural Engineering, Mechanics and Materials Seminar Series in Civil and Environmental Engineering, Georgia Tech, October 19, 2015, Atlanta, GA October 2015

- "Multiscale materials by design - connecting simulation, design, synthesis," Society of Engineering Science - 52nd Annual Technical Meeting, keynote lecture, Texas A&M University, October 28, 2015, College Station, TX October 2015
- "Modeling, Design, 3-D Printing of Multiscale Materials and Structures," ASCE Continuing Education, Dec. 2, 2015 December 2015
- “Building a Resilient World Through Big Engineering” MIT Club of New Jersey, May 11, 2016, in Newark, NJ May 2016
- “Merger of Structure and Material for Materials By Design: Comparative Bottom-up Analysis and Manufacturing of Hierarchical Materials," Talk at the ONR Life Sciences and Bioengineering Biomaterials and Bionanotechnology Program Review, Aug. 1, 2016, Washington, DC August 2016
- “Theory in biomaterials," Biomaterials: Tools and Foundry Workshop, August 2-3, 2016, Arlington, VA August 2016
- “Computational Design of Smart Materials: Multiscale Modeling,”-Chemical Heritage Foundation Innovation Day 2016, September 12-13, 2016, Philadelphia, PA
- September 2016
- "Multiscale Smart Materials by Design - Connecting Simulation, Design, Synthesis across Multiple Scales" Keynote Presentation at SMASIS Conference, Sept. 30, 2016, Stowe, VT. September 2016
- SES Conference at University of Maryland, talk, "De novo materials design – computation synthesis, characterization" October 2016
- “Multiscale smart materials by design - connecting simulation, design, synthesis across multiple scales,” Stookey and Development Excellence Awards, Corning, November 3, 2016, Corning, NY November 2016
- “Biomanufacturing,” MIT-ILP R&D Conference, November 16, 2016, Cambridge, MA November 2016
- “Nano Materials and Engineering Structures," The Hidden Infrastructure Symposium: Department of Chemical Engineering, Northeastern University, December 8, 2016, Boston, MA December

Technical part

Summary: For this project we have closely collaborated with Dr. Naik at AFRL to merge the computational and experimental effort to investigate the biomechanics of Nvjp-1 protein and to predict the pH and ionic effect on nanostructure and hydrodynamic properties of the protein and its assemblies. The Nvjp-1 protein is a key component in the jaws of Nereis virens, a species of marine worm. It contains over 25 mol% of histidine, which is believed to play a key role in the metal-coordinated crosslinking responsible for the structural stability and exceptional mechanical performance of the worm jaw. Understanding the nanoscale mechanism behind this crosslinking and its pathway in affecting the macroscopic mechanical behavior of the material is crucial to develop new bio-inspired mechanomutable materials based on Nvjp-1. Here, we use a combination of multiscale modeling and experimental synthesis to understand the behavior of this heterologous-expressed protein from the nano- to the macroscale. We have built a bottom-up molecular-based model, which includes electronic-based density functional theory calculations, atomistic simulation of the nanoscale properties with replica exchange molecular dynamics, and an elastic network model for describing the macroscale behavior at different pHs. This multiscale modeling supports the experimental synthesis of a photo-crosslinked Nvjp-1 hydrogel by proving both the nanoscale mechanisms and mechanical behavior predictions. Our theoretical results have been compared with experiments and we find good agreement with the experimental observations, showing that Nvjp-1 forms a more compact structure in the presence of Zn2+ ions with a suitable pH environment, leading to the formation of more stable intra-molecular metal-coordinated crosslinks. These metal-coordinated crosslinks induce nanoscale aggregation of Nvjp-1, which is responsible for the hydrogel contraction observed in experiments and predicted by the model.

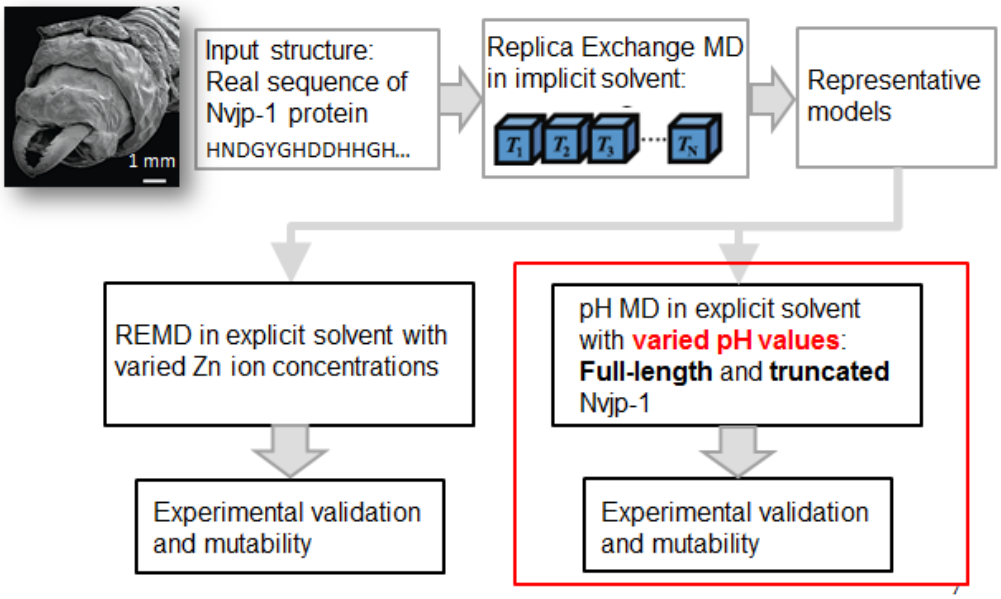

Figure 1. Illustration of simulation protocol of ionic and pH effects on protein structure and material properties study.

Main conclusion: To be more specific, we provide a complete multiscale modeling framework and experimental synthesis of a new bio-inspired hydrogels based on Nvjp-1 protein. The jaws of Nereis virens are condensed proteinaceous structures whose mechanical properties are tuned by coordination with transition metal cations, particularly Zn2+. Nereis virens is a marine organism and the dehydration during biosynthesis must occur in an aqueous environment. Since the removal of bulk water from the newly synthesized protein hydrogel cannot utilize evaporation, it is possible that the

contraction behavior observed in this study mimics an as yet unknown natural mechanism for dehydration of worm jaw material as it matures into a final functional form. The contraction of acid-swollen Nvjp-1 hydrogels is not dependent on the type of cation present in the salt. In fact, the initial driving force for removing bulk water from the hydrogel is likely due to charge screening of protonated histidine by the anion. The type of cation present in the salt seems to play a role in the degree of contraction experienced by the hydrogel, where Zn2+ treatment consistently yields a more compact structure compared to that seen with Na+. Our DFT calculations show a stronger interaction at crosslinking sites arising from the presence of Zn2+ ions, for which a three-coordinated crosslinking is slightly preferred, providing the most fundamental insight of the mutable mechanics of such biopolymer material. In addition, our atomistic model of the Nvjp-1 protein provides a better understanding of this phenomenon, and predicts that the Nvjp-1 has different mechanical response in different solutions with various ion concentrations. Structurally and mechanically tunable properties of Nvjp-1 are demonstrated with this model and compared against the experiments. We have calculated SASA of Nvjp-1 with the atomistic model, and have found that the SASA of Nvjp-1 decreases as the Zn2+/protein ratio increases. We have also calculated the radius of gyration to measure the size of Nvjp-1, and the results show that a more compact structure is formed in the presence of Zn2+ ions. These results show the consistent trend for solubility as with the values measured in the experiments. Our coarse-grained model of Nvjp-1 provides mesoscopic insights of it mechanical response, which demonstrates that it can adapt to shapes very different from its initial states by generating large mechanical deformations, providing opportunities to predict and design composite materials of active mechanical functions. Our results suggest that metal-coordinated crosslinks play a significant role in achieving the characteristic properties of this protein material.

Our study shows that Nvjp-1 provides an excellent example of mechanomutable protein material to investigate. By integrating multiscale analysis and experimental validation, we can learn the fundamental material science concepts at different scales from the quantum level of bond formation, to the atomistic scale protein folding and mesoscopic scale swelling and contraction in different chemical conditions. Our multiscale modeling provides the most comprehensive understanding of the formation, mechanical behavior and the tunable function of such protein materials under changing conditions. Inspired by Nvjp-1, we will use such computational modeling tool for rational polymer material design with desired tunable mechanical functions, which provides the rational way to fully program the mechanical response of the material in different conditions and is missing in most previous studies.

This study provides fundamental insight into mutable mechanical properties of Nvjp-1 and other proteins with metal-coordinated bonds from a bottom-up perspective. It also provides an opportunity to synthesize biomaterials with mutable properties in the presence of metal-coordinated crosslinks. Additionally, these pH-sensitive materials can be used for the design of bio-inspired adaptive materials for chemical sensing in cyber-physical systems or for active control of the deformation and motion of soft robotics, as it is shown in our large-scale simulations from which plant coil behavior and cypraea-like geometries are generated.